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Indoor formaldehyde removal over CMK-3

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Abstract

The removal of formaldehyde at low concentrations is important in indoor air pollution research. In this study, mesoporous carbon with a large specific surface area was used for the adsorption of low-concentration indoor formaldehyde. A mesoporous carbon material, CMK-3, was synthesized using the nano-replication method. SBA-15 was used as a mesoporous template. The surface of CMK-3 was activated using a 2N H₂SO₄ solution and NH₃ gas to prepare CMK-3-H₂SO₄ and CMK-3-NH₃, respectively. The activated samples were characterized by N₂ adsorption-desorption, X-ray diffraction, and X-ray photoelectron spectroscopy. The formaldehyde adsorption performance of the mesoporous carbons was in the order of CMK-3-NH₃ > CMK-3-H₂SO₄ > CMK-3. The difference in the adsorption performance was explained by oxygen and nitrogen functional groups formed during the activation process and by the specific surface area and pore structure of mesoporous carbon.

Keywords: low-concentration formaldehyde, mesoporous carbon, sulfuric acid, ammonia, activation, adsorption

Introduction

Currently, people spend more than 80% of their daily life indoors and are exposed to serious health risks due to indoor air pollution. In particular, the increased airtightness required for energy saving results in the accumulation of pollutants in less-ventilated indoor air. Sick building syndrome causing throat and nasal pains, headache, nausea, and vomiting due to indoor air pollution has become an important social issue with the increasing desire to improve the quality of life [1-3].

Formaldehyde is a representative indoor pollutant that is emitted from indoor furniture paint and floor materials. Formaldehyde has been categorized as a group 1 carcinogen by the International Agency for Research on Cancer [4]. Therefore, technology for removing formaldehyde is of great importance [5].

Adsorption, scrubbing, and advanced oxidation have been applied to remove volatile organic compounds, such as formaldehyde. In particular, adsorption using activated carbon is a method used most widely for removing formaldehyde [6]. Although the adsorption performance of activated carbon is excellent, it is not very efficient for the adsorption of polar species, such as formaldehyde.

Therefore, research is being carried out to develop more efficient adsorbents for formaldehyde [7].

Recently, the synthesis and application of ordered mesoporous carbons with a variety of structures, e.g., CMK-1, CMK-3, and CMK-5, have attracted considerable attention [8-11]. These ordered mesoporous carbons have been synthesized by carbonizing mesoporous silica materials, such as MCM-48, SBA-15, and KIT-6, and then by removing the silica template. Ordered mesoporous carbon is expected to have an extensive potential in a range of applications because of the uniform pore size, large specific surface area, and large pore volume [12]. These materials are considered to have a potential for applications to other fields, such as heterogeneous catalysis and host-guest chemistry [13-16]. In particular, CMK-3, based on SBA-15, which is easy to synthesize, is expected to be useful not only as an adsorbent but also as a catalyst substrate [12].

In this study, CMK-3 was applied for the first time to the adsorption of formaldehyde. The effect of modifying the surface of CMK-3 via a range of activations to improve the formaldehyde removal efficiency was evaluated.

Experimental details

Synthesis of CMK-3

An ordered mesoporous carbon, CMK-3, was prepared using the nano-replication method. Mesoporous silica

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SBA-15 was used as a template. A carbon precursor solution was prepared by dissolving 1.25 g of sucrose in a mixture containing 4 g of deionized water and 0.14 g of H_2SO_4 . The solution was allowed to infiltrate into the mesopores of the silica template. The mixture was dried at 100°C for 6 h. The impregnation and drying procedures were repeated twice using 66% sucrose. The carbonization was carried out at 900°C for 3 h under a nitrogen flow. Finally, CMK-3 was obtained by removing the silica matrix using an HF solution.

Ammonia and sulfuric acid treatments were applied to upgrade the characteristics of CMK-3. The ammonia treatment was performed by inserting CMK-3 into a reactor maintained at 900°C and allowing ammonia gas to flow through the reactor at a flow rate of 50 ml/min for 2 h. The reactor was purged for another 1 h with nitrogen gas at a flow rate of 50 ml/min. CMK-3, which was treated with ammonia in this way, is referred to as CMK-3- NH_3 .

The method of the sulfuric acid treatment of CMK-3 is as follows: CMK-3 was immersed in a 2N sulfuric acid solution prepared by using 95% sulfuric acid. The solution was stirred for 3 h at room temperature. The solution was then filtered, and the filtered sample was immersed in 100 g of distilled water and stirred for 1 h. This filtration and washing procedure was repeated at least ten times to neutralize the sample. The washed sample was dried for 24 h in an oven maintained at 110°C . The CMK-3 treated with sulfuric acid is referred to as CMK-3- H_2SO_4 .

Characterization of mesoporous carbons

X-ray diffraction [XRD] was carried out in reflection mode using a Rigaku D/MAX-2200 Ultima diffractometer (Rigaku International Corporation, Tokyo, Japan) equipped with Cu $K\alpha$ radiation at 30 kV and 40 mA. N_2 adsorption-desorption isotherms were collected on a Micromeritics Tristar system (Micromeritics Instrument Corporation, Chiba, Japan) at liquid N_2 temperature. The specific BET surface area was calculated from the adsorption branches in the relative pressure (P/P_0) range of 0.05 to 0.20. The pore size distribution curves were obtained from the adsorption branches using the BJH method.

X-ray photoelectron spectroscopy [XPS] measurements were performed using an AXIS Nova spectrometer (Kratos, Inc., NY, USA). A monochromatic Al $K\alpha$ (1,486.6 eV) of X-ray source and 40 eV of analyzer pass energy were used under ultra-high vacuum conditions (5.2×10^{-9} Torr).

Adsorption of formaldehyde

The adsorption experiments were carried out using the method described in the literature [17]. The 100-ppm

formaldehyde produced by Union Inc. was used in this study. A 10-L aluminum bag (to prevent oxidation by sunlight) was cleaned with N_2 gas and emptied using a vacuum pump. After introducing formaldehyde into the bag, N_2 gas was added to adjust the formaldehyde concentration to 1 ppm. Subsequently, 0.07 g of mesoporous carbon, which had been dried in advance for 24 h in an oven maintained at 100°C to remove the influence of moisture, was inserted into the aluminum bag. The temperature was controlled at 30°C using an incubator during the adsorption process to avoid any temperature dependency [17]. The sample bags were agitated in a shaking incubator to promote gas-solid mixing.

The amount of formaldehyde adsorbed at 0, 10, 40, and 80 min was measured using a formaldehyde analyzer (4000Series; Woori Industrial System Co., Ltd., Cheongwon-gun, South Korea).

Results and discussion

Characterization of mesoporous carbons

Figure 1 shows XRD patterns of CMK-3, CMK-3- H_2SO_4 , and CMK-3- NH_3 . The low-angle and high-angle patterns of XRD showed that CMK-3 and CMK-3- H_2SO_4 had a typical 2D-hexagonal structure, whereas the ordered mesostructure of CMK- NH_3 was comparatively deconstructed.

Table 1 lists the physical properties of mesoporous carbon used in this study. The specific surface area of CMK-3 was $1,178 \text{ m}^2/\text{g}$. The specific surface area decreased slightly to $1,002 \text{ m}^2/\text{g}$ after a treatment with sulfuric acid, whereas it increased considerably to $1,663 \text{ m}^2/\text{g}$ upon a treatment with ammonia. Figure 2 shows the nitrogen sorption isotherms and pore size distributions of mesoporous carbon. Figure 2a shows the nitrogen sorption isotherms for CMK-3, CMK-3- H_2SO_4 , and CMK-3- NH_3 . All the samples showed typical type IV isotherms of mesoporous materials under a relative pressure (P/P_0) of 0.5. Table 1 shows that CMK-3 has mesopores with a pore size of 3.8 nm. These mesopores were maintained after a treatment with sulfuric acid. When CMK-3 was treated with ammonia, the mean pore size decreased to 3.1 nm. Treatment with ammonia is a high-temperature (900°C) process that generates micropores causing a large increase in surface area and a decrease in average pore size. On the other hand, most of the mesoporous CMK-3 were maintained after the ammonia treatment.

Table 2 lists the elemental surface compositions obtained by XPS. CMK-3- H_2SO_4 showed higher C and O contents than CMK-3, whereas CMK-3- NH_3 had lower C and O contents than CMK-3. N was detected in CMK-3- NH_3 , but not in CMK-3. This suggests that a sulfuric acid treatment and ammonia treatment have added oxygen and nitrogen functional groups, respectively, on the CMK-3 surface.

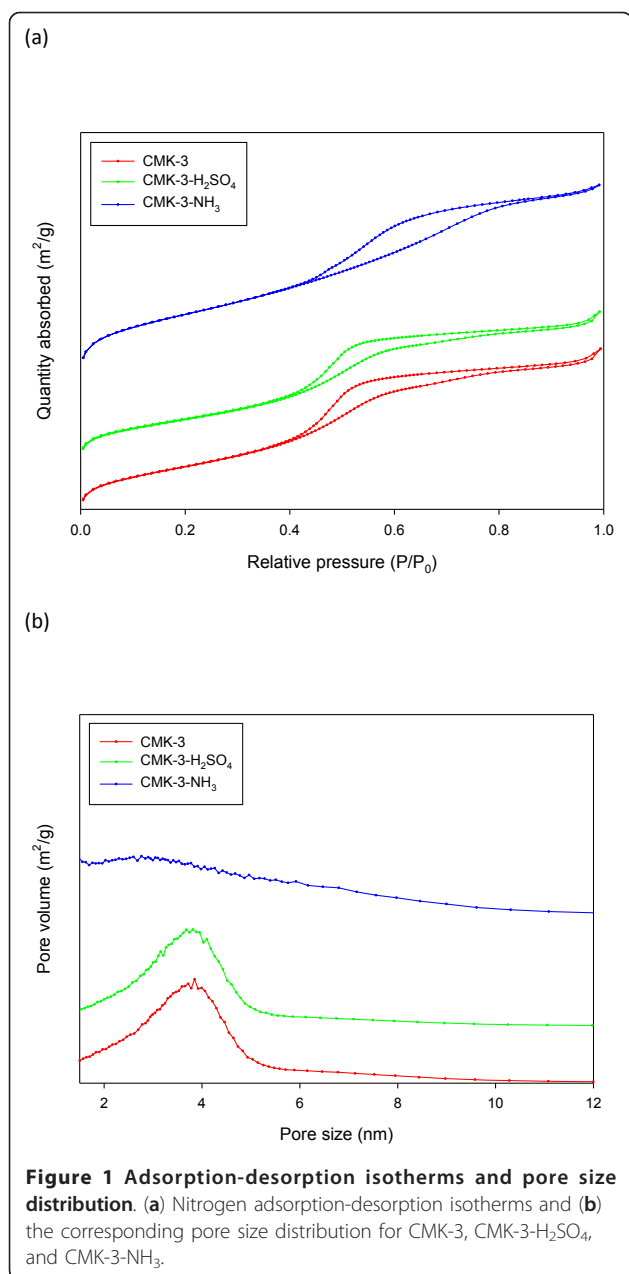
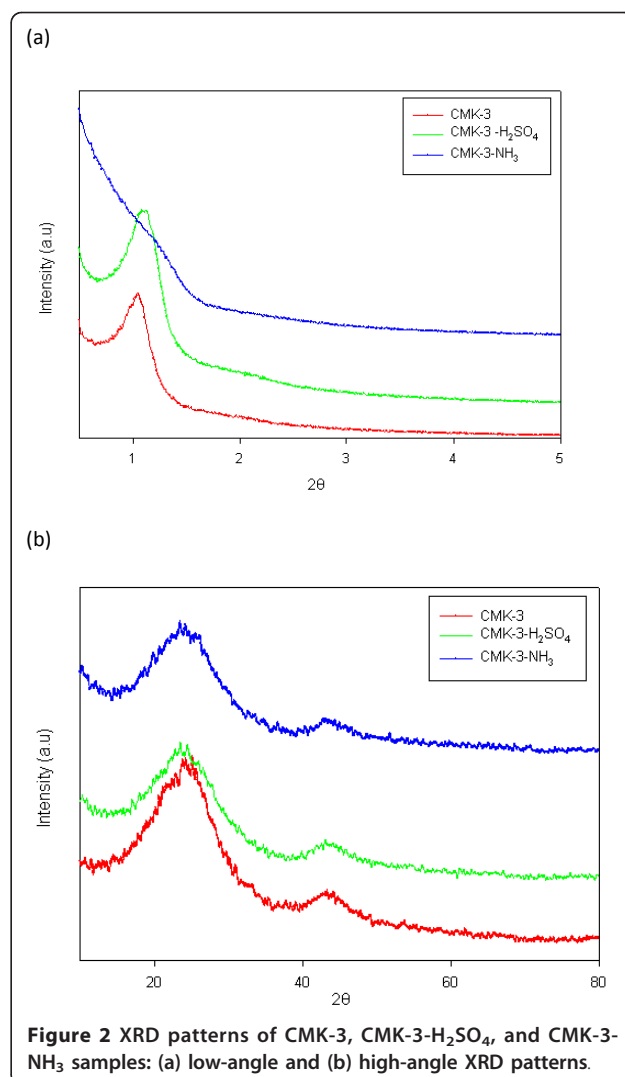


Figure 3 shows the O1s and N1s spectra obtained from XPS. The O1s spectra (Figure 3a) showed four peaks even though the intensity of each peak was dependent on the treatment method. Generally, the



peaks appeared at the binding energy levels of 531.1 (± 0.5), 532.8 (± 0.5), 535.1 (± 0.5), and 537.6 (± 0.5) eV, representing C-OH, C=O, O₃, and O₄, respectively [18]. The C-OH peak was shown to increase dramatically after the sulfuric acid treatment. The N1s spectrum was detected only for CMK-3-NH₃ (Figure 3b). N1s peaks were observed at two binding energy levels. The peaks appearing at 399.2 (± 0.5) and 400.9 (± 0.5) eV represent atomic N and pyridine-like N, respectively [19].

Table 1 Physicochemical properties of various CMK-3 materials

Sample	Specific surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (nm)	Micropore area (m ² /g)	Micropore volume (cm ³ /g)
CMK-3	1178	1.28	3.8	142	0.05
CMK-3-H ₂ SO ₄	1002	1.14	3.8	93	0.03
CMK-3-NH ₃	1633	1.55	3.1	394	0.16

Table 2 Elemental surface composition of various CMK-3 materials

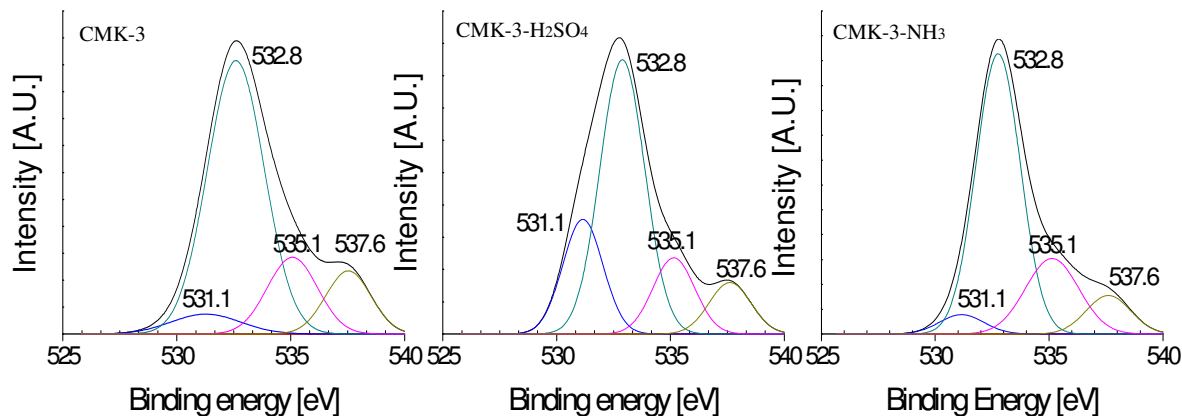
Sample	Atomic surface concentration obtained by XPS (%)		
	C	O	N
CMK-3	96.67	2.11	-
CMK-3-H ₂ SO ₄	97.18	2.82	-
CMK-3-NH ₃	94.49	1.43	3.66

Adsorption of formaldehyde

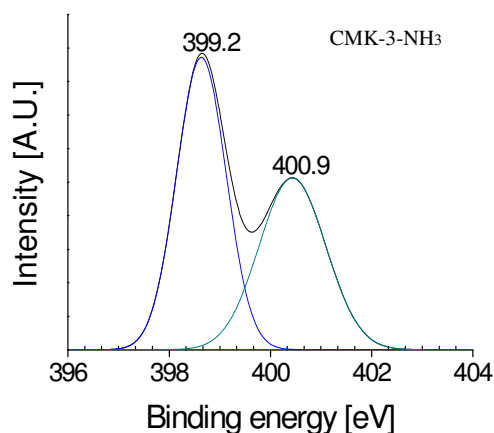
Figure 4 shows the results of the formaldehyde adsorption experiments using CMK-3, CMK-3-H₂SO₄, and CMK-3-NH₃. Adsorption occurred most rapidly in the first 10 min and then slowed down gradually. Without

treatment, CMK-3 showed a high adsorption efficiency > 50% owing to its large specific surface area. CMK-3-H₂SO₄ showed slightly improved adsorption performance compared to CMK-3 despite its smaller specific surface area than CMK-3, which was attributed to the highest surface O concentration resulting from an increase in oxygen functional groups. Lee et al. [20] reported that the increase in oxygen functional groups on sludge char through activation increased the formaldehyde adsorption efficiency, which is in good agreement with the present results.

CMK-3-NH₃ showed the highest formaldehyde adsorption performance. Kim et al. [17] examined the effect of the addition of amine groups to mesoporous

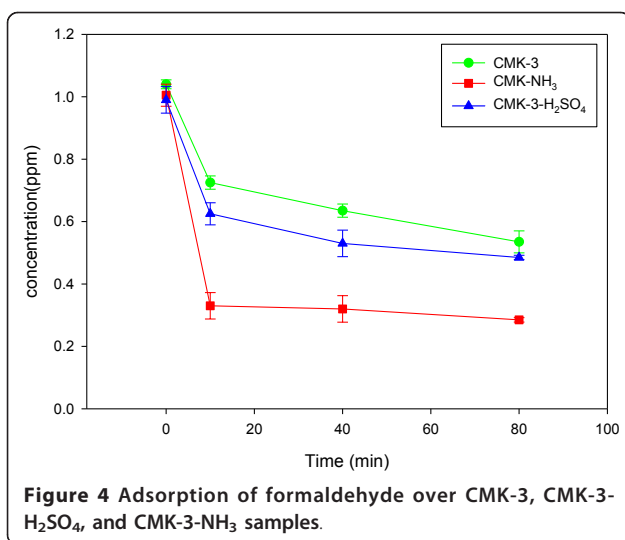


(a)



(b)

Figure 3 XPS spectra of CMK-3, CMK-3-H₂SO₄, and CMK-3-NH₃ samples: (a) O1s spectrum and (b) N1s spectrum.



materials and reported that the addition of amine groups could enhance formaldehyde adsorption. Srisuda and Virote [21] also reported improved formaldehyde adsorption performance of mesoporous materials obtained by the introduction of amine groups. They argued that the interaction between formaldehyde and ammonia contributed to the increased adsorptivity. Therefore, the improved formaldehyde adsorption performance observed in the present study was attributed to the increase in nitrogen functional groups resulting from an ammonia treatment. The increase in specific surface area due to the formation of micropores might also have contributed to the increased adsorptivity.

Conclusions

CMK-3 with a uniform pore structure, large specific surface area, large pore size, and large pore volume was applied to the adsorption of formaldehyde. CMK-H₂SO₄ and CMK-NH₃ were also obtained by a treatment with sulfuric acid and ammonia, respectively. CMK-3 and CMK-3-H₂SO₄ had a 2D-hexagonal structure, whereas CMK-3-NH₃ showed a somewhat disordered structure due to partial destruction of the ordered mesostructure. On the other hand, CMK-3-NH₃ had the largest specific surface area and pore volume. XPS showed that only CMK-3-NH₃ had nitrogen functional groups, whereas CMK-3-H₂SO₄ had the largest amount of oxygen functional groups. The order of the adsorption performance against formaldehyde was CMK-3-NH₃ > CMK-3-H₂SO₄ > CMK-3. This was attributed to the combined effects of nitrogen and oxygen functional groups and the specific surface area.

Abbreviations

XRD: X-ray diffraction; XPS: X-ray photoelectron spectroscopy.

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Authors' contributions

HBA, MJY, JMK, MJ, KJ, SHP, SSK participated in some of the studies and in drafting the manuscript. YKP conceived of the study and participated in all experiments of this study. Also, YKP prepared and approved the final manuscript. All authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

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